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A symmetric hydrogen bond revisited: Potassium hydrogen maleate by variable temperature, variable pressure neutron diffraction and plane-wave DFT methods**

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Abstract

The symmetric hydrogen bond in potassium hydrogen maleate has been re-investigated by diffraction and computational methods. Single crystal neutron diffraction under varying temperature (30–295 K) and pressure (ambient–4 kbar) confirmed the crystallographically-constrained symmetric disposition of the hydrogen atom in the short, strong hydrogen bond for each of eight sets of (p, T) conditions. Plane-wave DFT calculations show the hydrogen atom still to occupy this symmetric position even when crystallographic symmetry is removed, in stark contrast to the results from isolated molecule *ab initio* calculations. These results demonstrate that the symmetric (or close to symmetric) nature of this hydrogen bond is intrinsic.

1. Introduction

Hydrogen bonding is a donor-acceptor interaction of the form $D-H\cdots A$ where a covalent bond is maintained with the donor atom D and a weaker hydrogen bond is formed with the acceptor atom, A [1]. It is widely accepted that the hydrogen atom sits in a double minimum potential energy well. However, as the hydrogen bond gets stronger, the distance between the two minima decreases until in the case of a strong hydrogen bond, the barrier between the two disappears leaving a single flattened potential well. In this way, short hydrogen bonds frequently exhibit single minimum or low barrier potentials, often with evidence of quasi-covalent character as indicated from the critical point behaviour in these bonds when subjected to topological analyses of the electron density as determined from high resolution X-ray diffraction studies [2].

Recent variable temperature neutron diffraction studies of molecular structures containing hydrogen bonds have shown that the hydrogen atom of interest can exhibit interesting behaviour under varying conditions [3], [4], [5], [6], [7], [8], [9], [10] and [11]. The work here extends this to include variable pressure studies and represents one of the first systematic (p, T) studies of a molecular hydrogen bonded system by single crystal neutron diffraction.

The compound studied here is potassium hydrogen maleate ($KH(OOC-CH \cdot CH-COO)$). The hydrogenmaleate ion [12] contains a short strong hydrogen bond where the position of the hydrogen atom is sensitive to the crystallographic environment, and has been widely studied with varying cations. The hydrogen atom was observed as centred within the hydrogen bond in the case of the imidazolium salt [13] and [14] but occupying an asymmetric position when the cation is calcium [15]. Notably, the centring of the hydrogen bond in the former compound is not constrained by crystallographic symmetry. Evidence for the centring of the hydrogen atom in the solid state in the title compound, potassium hydrogen maleate, was first observed from X-ray diffraction studies where the electron density was observed to be consistent with that of a centred proton [16] and [17]. The compound crystallises in the orthorhombic space group $Pbcm$ with four molecules in the unit cell. In this space group, the anion is situated about a mirror plane, the hydrogen atom sitting on the

mirror plane and thus constrained to be centred, in the absence of disorder. The molecular symmetry in this situation is C_{2v} . The observation of a centred proton was supported by optical spectroscopy [18], [19] and [20] and isotope effects in NMR measurements [21]. Neutron diffraction studies confirm these findings [22] and the proton has subsequently been found to be centred at 300, 14 and 5 K [23]. Attempts have been made to define a hydrogen bond potential on the basis of band assignments in inelastic neutron scattering (INS) spectra [23]. However, the derived potentials are by no means of a general nature and the physical basis of these is not obvious. Such empirical fits can be used to explain the INS data but do not yield wider interpretations of, for example, the diffraction data we are considering here.

In addition to these experimental methods, ab initio molecular orbital calculations [24], [25] and [26] have also previously been applied to the maleate anion. These concurred that the symmetric (C_{2v}) structure is a transition state and the asymmetric (C_s) structure a minimum, but that the energy difference between the two stationary points is smaller than the zero-point energy correction. That is to say, for any experimental measurement, the hydrogen bond will appear symmetrical, regardless of the small hump at the bottom of the potential well.

However, as the experimental results show that the position of the proton in the hydrogen bond is affected by the crystallographic environment for this and other short hydrogen bond systems, more may be gained by moving beyond the isolated molecule simulation. This can be achieved by using an alternative calculation method, such as plane-wave DFT (PW-DFT), to simulate the entire unit cell within periodic boundary conditions [27]. As well as performing full geometry optimisations for the lattice in the absence of crystallographic symmetry constraints, we have also used PW-DFT calculations to map out the shape of the hydrogen bond potential energy surface, both within the unit cell environment and for a ‘quasi-isolated’ hydrogen maleate anion in a large, otherwise empty, supercell. In this way we hope to demonstrate that any change in the intramolecular hydrogen bond potential can be positively attributed to a change in phase from gas to solid, rather than a possible bias in the calculation method employed.

2. Experimental

2.1. Neutron diffraction

The crystals were grown by slow evaporation from aqueous ethanol solution. Data were collected on the SXD instrument at the ISIS spallation neutron source [28], using the time-of-flight Laue diffraction method [28],[29] and [30]. The crystals were placed into a ‘null-coherent-scattering’ titanium-zirconium alloy pressure cell, which is mounted onto a closed cycle refrigerator on a vertical (ω) rotation device. The pressure is applied using helium gas and the open geometry of the cell allows the $>2\pi$ Sr solid angle coverage of the SXD instrument to be exploited. The pressure cell has an internal diameter of ~ 1.7 mm, which limits the size

of crystals that it is possible to use. A multiple crystal sample technique was employed [31], using three single crystals, each of approximate dimension $1.5 \times 1 \times 1 \text{ mm}^3$. A total of three frames were collected at each temperature and pressure, each containing information from all eleven detectors, to give representative three-dimensional data sets containing between 580 and 1154 unique reflections, used to refine the structural model of 57 parameters including anisotropic ADPs.

2.2. Isolated molecule calculations

For completeness, we have performed ab initio molecular orbital calculations using the Gaussian 98 program[32] on the isolated hydrogen maleate anion in C_{2v} and C_s symmetry, with results consistent with those already in the literature [24], [25] and [26]. The two stationary points found were characterised by vibrational frequency calculations at the HF/6-31G* level.

2.3. Plane-wave DFT calculations

2.3.1. Lattice calculations

A set of plane-wave (i.e., periodic) DFT calculations was undertaken using the VASP 4.4 simulation package[33] for the unit cell of potassium hydrogen maleate (i.e., all 48 atoms). The atomic positions and lattice vectors obtained from the low-temperature (20 K) neutron diffraction study were used as the initial starting point. All optimisation steps were performed in the absence of symmetry constraints (i.e., in space group P1) to allow the intramolecular hydrogen bond coordinates to optimise freely. The wavefunction was generated using a series of pseudopotentials (in effect describing the atomic cores) and plane waves (to describe the valence electrons) expressed at an energy cut-off of 396 eV. The generalised gradient approximation (GGA) PW91 modelled the electronic exchange and correlation potentials. Integrations over the non-symmetrised Brillouin zone were performed using one k -point positioned at the Γ -point. The first set of calculations performed established the volume of the periodic cell that gave rise to the lowest lattice energy. Subsequent fixed-volume calculations alternated between optimisation of the unit cell parameters and atomic positions until convergence was achieved. (N.B. as the potential energy surface was found to be very shallow, a more stringent set of optimisation criteria (forces to within $0.01 \text{ eV } \text{\AA}^{-1}$ and SCF energy convergence to within $1 \times 10^{-5} \text{ eV}$) than the program default settings were employed.)

2.3.2. Potential energy surface calculations

In addition to the full geometry optimisation calculations performed using PW-DFT calculations on the unit cell of potassium hydrogen maleate, we have also run a series of calculations to map out the shape of the hydrogen bond potential energy surface. In these calculations, all four bridging hydrogen atoms (one in each of the independent molecules employed in this calculation) were held at fixed distances from the left-hand side oxygen atoms, with the rest of the structure free to optimise. The energy of the system was noted as $r_{\text{O-H}}$ was varied from 1.08 to 1.32 Å in increments of 0.02 Å. Similar calculations were also performed for one hydrogen maleate anion located at the centre of a $14 \times 14 \times 14$ Å supercell, run at a higher energy cut-off of 495 eV. Such a large supercell effectively creates a ‘quasi-isolated’ molecule (although as the structure is anionic, monopole-monopole interactions between neighbouring cells, which decay slowly at a rate of $1/r$, cannot be completely dismissed). If the potential energy surface generated for this model displays the same general features as those obtained in the Gaussian ab initio MO calculations (i.e., the C_s geometry lower in energy than the C_{2v}), then the stabilisation of the C_{2v} geometry in the solid phase must be attributed to packing effects exerted by the crystallographic lattice.

3. Results and discussion

3.1. Neutron diffraction

The molecular geometry of the hydrogen maleate ion is shown in Fig. 1, with the hydrogen atom involved in hydrogen bonding located on the mirror plane. The position of this atom is unaltered by the variation of temperature or pressure (Table 1). As expected, the unit cell dimensions are contracted on application of pressure, but there are no significant changes in bond lengths. The thermal ellipsoids become larger with increasing temperature, but there is no anomalous behaviour of these (which would indicate an inadequacy in the model being used). The molecule is planar and this remains so as pressure is applied (Fig. 2), with no anomalous out-of-plane motions indicated by the refined atomic displacement parameters.

Table 1. Experimental hydrogen bond geometry in potassium hydrogen maleate as a function of temperature and pressure

P (kbar)	0	0	2	2	2	4	4	4
T (K)	20	300	50	125	200	50	125	200
$\text{O1}\cdots\text{O1}'$	2.430(2)	2.425(3)	2.430(2)	2.430(2)	2.419(3)	2.428(2)	2.428(2)	2.425(3)
O1-H1	1.216(2)	1.214(2)	1.216(1)	1.216(2)	1.210(2)	1.215(1)	1.215(2)	1.214(2)
$\text{O1-H1}\cdots\text{O1}'$	175.9(4)	175.3(5)	176.1(5)	174.9(6)	177.3(8)	175.6(5)	175.6(6)	174.5(9)

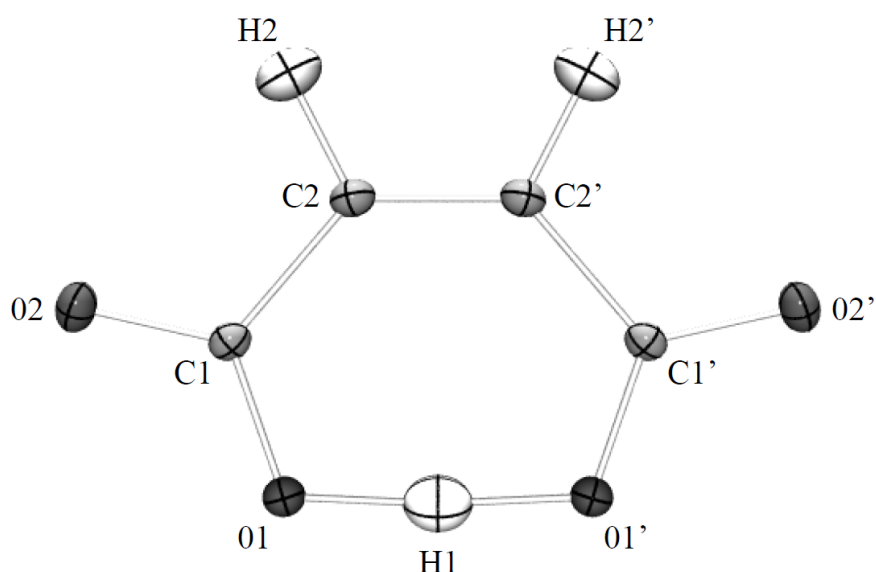


Figure 1. A view of the hydrogen maleate ion as determined from single crystal neutron diffraction at 125 K and 2 kbar, showing the atomic numbering. The prime indicates the atoms which are related by a mirror plane, upon which hydrogen atom H1 sits.

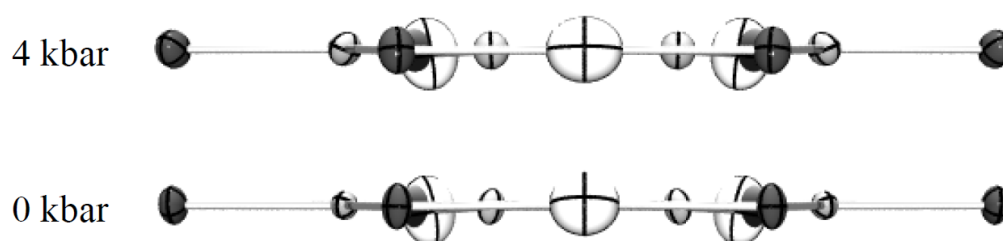


Figure 2. The planarity of the hydrogen maleate ion. The 0 kbar structure was determined at 20 K and the 4 kbar at 50 K. Notably, there are no ‘enhanced’ thermal motions perpendicular to the ring plane, giving no indication of any incipient non-planarity of the structure.

In order to investigate further the short hydrogen bond, a series of difference Fourier maps for the hydrogen maleate ion were calculated from our neutron data, to reconstruct the proton density. These show that the hydrogen atom involved in hydrogen bonding has a similar size and shape to the hydrogen atoms attached to carbons (Fig. 3) and we see no evidence for asymmetry of the proton in the hydrogen bond. We contrast this finding with that recently reported in the case of potassium hydrogen dichloromaleate [34] and [35], in which

the hydrogen bonds are intermolecular. In the latter case the structure was refined in the acentric space group P1 but with the heavy atoms constrained to be centrosymmetric, thus creating a pseudosymmetric system in which the hydrogen atoms are found to be asymmetrically positioned. We see no evidence from Fig. 3 that would suggest adopting a similar model here.

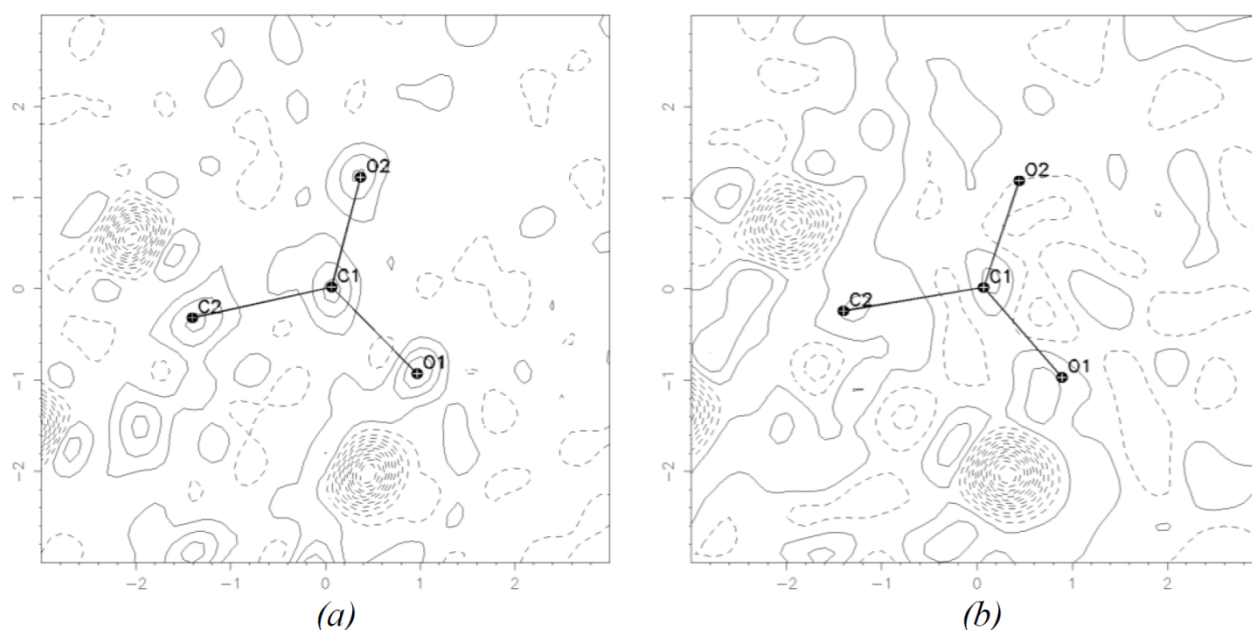


Figure 3. Difference-Fourier density maps for the hydrogen maleate ion in potassium hydrogen maleate, phased using just the heavy atoms for the ambient pressure (a) 30 K case and (b) room temperature case. This shows the relative sizes and shapes of the density defining the hydrogen atoms in the maleate ion. The density trough (dashed contours) close to O1 defines the hydrogen bonded hydrogen atom and this does not appear elongated in either case. For comparison, the hydrogen atom involved in hydrogen bonding looks similar to the hydrogen atom bonded to the carbon atom (trough close to C2) for both temperatures.

3.2. Isolated molecule calculations

The results obtained for the C_{2v} and C_s structures of the hydrogen maleate anion were consistent with literature values [24], [25] and [26]; selected parameters from the B3LYP/6-311++G* calculations are reported in Table 2. The C_s structure (asymmetric H bond) is the global minimum, whilst the C_{2v} structure (symmetric H bond) is characterised as a transition state some 2.9 kJ mol^{-1} above the minimum (without zero-point energy correction).

Table 2. Summary of observed (ND - neutron diffraction, 20 K) and calculated parameters obtained for the hydrogen maleate anion and potassium hydrogen maleate crystal

	ND	B3LYP/6-311++G*	B3LYP/6-311++G*	PW-DFT
Lattice parameters (Å)				
<i>A</i>	4.513	–	–	4.538
<i>B</i>	7.729	–	–	7.769
<i>C</i>	15.957	–	–	16.022
α, β, γ	90.0	–	–	90.0
<i>V</i>	556.45	–	–	564.9
Symmetry	Pbcm	C _{2v}	C _s	P1
Geometric parameters (Å)				
C2–C2'	1.346	1.344	1.344	1.347
C1–C2 (C1'–C2')	1.499	1.515	1.502/1.526	1.484
C1–O1 (C1'–O1')	1.296	1.295	1.316/1.276	1.303
O1...O1'	2.429	2.413	2.489	2.407
O1...H1 (H1...O1')	1.215/1.215	1.207/1.207	1.052/1.440	1.201/1.209
Δ O–H	0.0	0.0	0.388	0.008
Energy				
Hartrees	–	–455.3558612	–455.356955	–
eV	–	–	–	–315.361938

3.3. Plane-wave DFT calculations

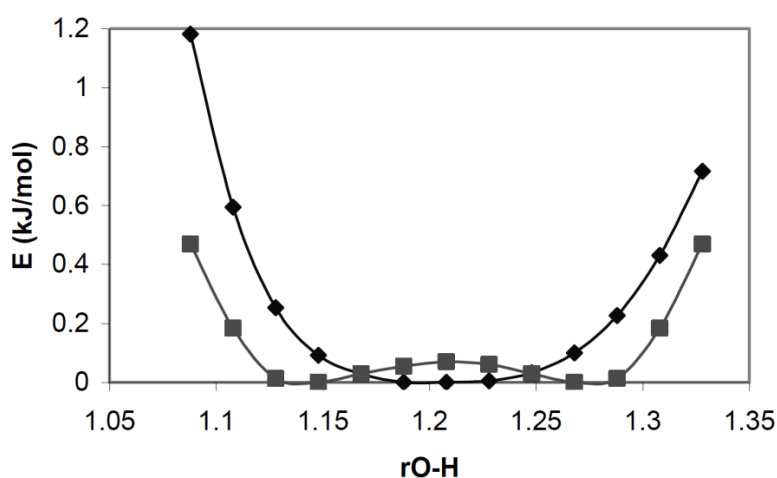
3.3.1. Lattice calculations

The results obtained from the PW-DFT calculations run for the potassium hydrogen maleate unit cell are given in Table 2. The first point to note is that the volume found to give rise to the lowest lattice energy is slightly larger than the experimental result. This is a common feature of DFT calculations that make use of GGA functionals; in our case the volume increase is only 1.5%, which translates to an increase in the three lattice vectors of no more than 0.04 Å. Although each optimisation step was performed in the absence of symmetry constraints, the geometric parameters obtained for each of the four complexes in the unit cell were consistent to three decimal places. The first geometry optimisation performed took the experimental (20 K) atomic coordinates as input, and the corresponding optimised structure placed the hydrogen atoms very close to the mid-point of the O...O bonds (see Table 2). With solid-state calculations, as there is currently not the same facility to characterise any stationary points found by determining analytic second derivatives via vibrational frequency calculations, it was not known if this symmetric structure represented a transition state or a minimum on the potential energy surface. Subsequently, two further geometry optimisations were performed with the four bridging hydrogen atoms shifted randomly towards one or other bonded oxygen atom to give bond lengths of 1.05 Å (i.e., a standard O–H bond) and the optimisation restarted. In both cases, the

hydrogen atoms returned to (or very close to) the midpoints of the hydrogen bonds, thus strongly suggesting the symmetric hydrogen bond represents the lowest energy point on the potential energy surface.

3.3.2. Potential energy surface scans

The slight asymmetry (0.008 Å, corresponding to just 2-3 times the experimental standard deviation for a bond of this type) found in the calculated structure (see Table 2) is likely to be an artefact of the very flat nature of the potential energy surface. As the two main criteria used to determine when a stationary point has been found in the calculation are changes in energy from one cycle to the next, and minimisation of forces (i.e., a levelling in the gradient of the potential energy surface), both criteria are easily fulfilled for systems with very shallow potential energy wells. In this respect, running a series of potential energy surface scans, where the change in energy of the total system is recorded as a particular parameter (in this case $r_{\text{O-H}}$) is varied, is perhaps more meaningful than a full geometry optimisation. The results obtained from the scans run for the unit cell and hydrogen maleate anion using PW-DFT are given in Fig. 4. From this it can be seen that, as is widely accepted, the potential energy surface for a strong hydrogen bond in the solid state is indeed a single flattened potential well. In contrast, however, we see that by attempting to break up the crystal lattice and isolate the hydrogen maleate anion (the results from the supercell calculations) the beginning of the return of the double well minimum potential is observed, which is consistent with the isolated molecule ab initio MO calculations. Thus, for the isolated hydrogen maleate anion, the calculations support the asymmetric hydrogen bond as the lowest energy structure, but for the potassium hydrogen maleate crystal, the periodic calculations show clear evidence of a flat potential energy surface, and consequently favour the symmetric intramolecular hydrogen bond. Our calculations therefore demonstrate that the change in phase from gas to solid fundamentally changes the shape of the intramolecular hydrogen bond potential from a double well with low transition state barrier to a single, broad minimum.



← **Figure 4.** Potential energy surfaces for the full unit cell (diamonds) and the quasi-isolated hydrogen maleate anion (squares) in a $14 \times 14 \times 14$ Å supercell. The calculations show a broad, flat surface for the unit cell, but a return to the double well minima surface when the crystal packing forces are removed. Energies are expressed per molecule.

4. Concluding remarks

We have demonstrated, by the use of ab initio molecular orbital calculations and plane-wave DFT calculations, that the nature of the intramolecular hydrogen bond potential for the hydrogen maleate anion changes as a consequence of state. In the gas phase (i.e., isolated molecule) an asymmetric (C_s) hydrogen bond is the lower energy arrangement, but in a crystalline environment with potassium counter-cations the potential energy well flattens to favour the symmetric (C_{2v}) bonding environment.

Although we have observed no change in the hydrogen atom position as a function of pressure, we have also shown that it is possible to carry out systematic investigations into the effects of variable temperature and variable pressure on molecular systems using single crystal neutron diffraction. Structural refinements and difference Fourier calculations give strong support to the model of a symmetric hydrogen atom, with no indication of asymmetry or disorder.

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